

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

**APPLICATION FOR LETTERS PATENT**

\* \* \* \* \*

**Chemical Vapor Deposition Methods Of  
Forming Barium Strontium Titanate Comprising  
Dielectric Layers**

\* \* \* \* \*

**INVENTOR**

**Cem Basceri  
Nancy Alzola**

**ATTORNEY'S DOCKET NO. MI22-1724**

TELEPHONE 332-6600

# Chemical Vapor Deposition Methods Of Forming Barium Strontium Titanate Comprising Dielectric Layers

## TECHNICAL FIELD

This invention relates to chemical vapor deposition methods of forming barium strontium titanate comprising dielectric layers, including such layers having varied concentration of barium and strontium within the layer.

## BACKGROUND OF THE INVENTION

As DRAMs increase in memory cell density, there is a continuing challenge to maintain sufficiently high storage capacitance despite decreasing cell area. Additionally, there is a continuing goal to further decrease cell area. One principal way of increasing cell capacitance is through cell structure techniques. Such techniques include three-dimensional cell capacitors, such as trench or stacked capacitors. Yet as feature size continues to become smaller and smaller, development of improved materials for cell dielectrics as well as the cell structure are important. The feature size of 256Mb DRAMs and beyond will be on the order of 0.25 micron or less, and conventional dielectrics such as  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  might not be suitable because of small dielectric constants.

Highly integrated memory devices are expected to require a very thin dielectric film for the 3-dimensional capacitor of cylindrically stacked or trench

structures. To meet this requirement, the capacitor dielectric film thickness will be below 2.5nm of SiO<sub>2</sub> equivalent thickness.

Insulating inorganic metal oxide materials (such as ferroelectric materials, perovskite materials and pentoxides) are commonly referred to as "high k" materials due to their high dielectric constants, which make them attractive as dielectric materials in capacitors, for example for high density DRAMs and non-volatile memories. Using such materials enables the creation of much smaller and simpler capacitor structures for a given stored charge requirement, enabling the packing density dictated by future circuit design. One such known material is barium strontium titanate.

TOP SECRET

## **SUMMARY**

The invention comprises in one aspect a chemical vapor deposition method of forming a barium strontium titanate comprising dielectric layer. A substrate is positioned within a chemical vapor deposition reactor. Barium and strontium are provided within the reactor by flowing at least one metal organic precursor to the reactor. Titanium is provided within the reactor. At least one oxidizer is also flowed to the reactor under conditions effective to deposit a barium strontium titanate comprising dielectric layer on the substrate. In one implementation, the oxidizer comprises  $H_2O$ . In one implementation, the oxidizer comprises  $H_2O_2$ . In one implementation, the oxidizer comprises at least  $H_2O$  and at least another oxidizer selected from the group consisting of  $O_2$ ,  $O_3$ ,  $NO_x$ ,  $N_2O$ , and  $H_2O_2$ , where "x" is at least 1. In one implementation, the oxidizer comprises at least  $H_2O_2$  and at least another oxidizer selected from the group consisting of  $O_2$ ,  $O_3$ ,  $NO_x$ , and  $N_2O$ , where "x" is at least 1.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is schematic diagram of an exemplary system usable in accordance with an aspect of the invention.

Fig. 2 a diagrammatic sectional view of a semiconductor wafer fragment in process in accordance with an aspect of the invention.

Fig. 3 is a diagrammatic sectional view of an alternate embodiment semiconductor wafer fragment in process in accordance with an aspect of the invention.

## **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

Fig. 1 diagrammatically illustrates but one chemical vapor deposition system 10 in accordance with but one implementation of a chemical vapor deposition method in accordance with an aspect of the invention. Such comprises an A precursor feed stream 12 and a B precursor feed stream 14. Such combine and feed to a vaporizer 16. An inert gas stream 18 can also

be provided to vaporizer 16 to facilitate flow of the vaporized precursors to a downstream chamber.

A chemical vapor deposition chamber 20 is connected downstream of vaporizer 16. Such includes a showerhead 22 for receiving and distributing gaseous precursors therein. A suitable wafer holder 24 is received within chamber 20. Oxidizer gas feed streams, for example two oxidizer feed streams C and D, are preferably provided upstream of the showerhead. Further, an additional inert gas feed stream 19 is shown positioned between the oxidizer feed streams and chamber. More or less feed streams with or without mixing might also of course be utilized. The deposition is preferably conducted at subatmospheric pressure, with a vacuum pump 26 and an exemplary valve 28 being diagrammatically illustrated for achieving a desired vacuum pressure within chamber 20. Further, the deposition may or may not be plasma enhanced.

In one example, and by way of example only, the A stream consists essentially of a mixture of Ba and Sr precursors (i.e., preferably about 50%-50% by volume), and the B stream consists essentially of Ti precursor(s). Example preferred deposition is by metal organic chemical vapor deposition (MOCVD) processes, with at least one oxidizer being provided within chamber 20 with suitable MOCVD precursors to deposit a desired barium strontium titanate comprising dielectric layer. Example precursors, and by way of example only, include:

Ba(thd) <sub>2</sub>	-	bis(tetramethylheptanedionate)
Sr(thd) <sub>2</sub>	-	bis(tetramethylheptanedionate)
Ti(thd) <sub>2</sub> (O-i-Pr) <sub>2</sub>	-	(isopropoxide)bis(tetramethylheptanedionate)
Ba(thd) <sub>2</sub>	-	bis(tetramethylheptanedionate)
Sr(thd) <sub>2</sub>	-	bis(tetramethylheptanedionate)
Ti(dmae) <sub>4</sub>	-	bis(dimethylaminoethoxide)
Ba(methd) <sub>2</sub>	-	bis(methoxyethoxyte, tetramethylheptanedionate)
Sr(methd) <sub>2</sub>	-	bis(methoxyethoxyte, tetramethylheptanedionate)
Ti(mpd)(thd) <sub>2</sub>	-	bis(methylpentanediol, tetramethylheptanedionate)
Ba(dpm) <sub>2</sub>	-	bis(dipivaloylmethanato)
Sr(dpm) <sub>2</sub>	-	bis(dipivaloylmethanato)
TiO(dpm) <sub>2</sub>	-	(titanyl)bis(dipivaloylmethanato)
Ba(dpm) <sub>2</sub>	-	bis(dipivaloylmethanato)
Sr(dpm) <sub>2</sub>	-	bis(dipivaloylmethanato)
Ti(t-BuO) <sub>2</sub> (dpm) <sub>2</sub>	-	(t-butoxy)bis(dipivaloylmethanato)
Ba(dpm) <sub>2</sub>	-	bis(dipivaloylmethanato)
Sr(dpm) <sub>2</sub>	-	bis(dipivaloylmethanato)
Ti(OCH <sub>3</sub> ) <sub>2</sub> (dpm) <sub>2</sub>	-	(methoxy)bis(dipivaloylmethanato)

Adducts (i.e., tetraglyme, trietherdiamine, pentamethyldiethylenetriamine), solvents (i.e., butylacetate, methanol, tetrahydrofuran), and/or other materials might be utilized with the precursors. By way of example only, and where the precursors include metal organic precursors, example flow rates for the various of such precursors include anywhere from 10 mg/min. to 1000 mg/min. of liquid feed to any suitable vaporizer.

A first aspect of the invention is described in connection with a chemical vapor deposition method of forming a barium strontium titanate comprising dielectric layer having a varied concentration of barium and strontium within the layer. By way of example only, an exemplary implementation is described with reference to Fig. 2. Fig. 2 depicts an

exemplary substrate 110 comprising a bulk monocrystalline silicon substrate 112. In the context of this document, the term "semiconductor substrate" or "semiconductive substrate" is defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above. An insulative layer 114, such as borophosphosilicate glass (BPSG) by way of example only, is formed over substrate 112. A conductive capacitor electrode layer 116, such as platinum or an alloy thereof by way of example only, is formed over layer 114.

Such substrate is placed within a chemical vapor deposition reactor. Plasma, remote or within the chamber, might be utilized. Barium and strontium are provided within the reactor by flowing at least one metal organic precursor to the reactor. Titanium is also provided within the reactor. By way of example only, exemplary precursors are as described above. At least one oxidizer is also flowed to the reactor. Conditions are provided within the reactor effective to deposit a barium strontium titanate comprising dielectric layer 118 on the substrate. In one preferred embodiment, the barium and strontium are provided within the reactor by flowing at least two metal organic precursors to the reactor, with one of the precursors comprising barium, and



another of the precursors comprising strontium. Such precursors might be fed to the reactor as separate flow streams, or as a mixture in a single flow stream, as depicted by Fig. 1 and described above with respect to stream 12.

In accordance with the invention, the oxidizer comprises at least one of  $H_2O$  or  $H_2O_2$ . Other oxidizers might also be utilized. In one aspect of the invention, the oxidizers comprise at least  $H_2O$  and at least another oxidizer selected from the group consisting of  $O_2$ ,  $O_3$ ,  $NO_x$ ,  $N_2O$ , and  $H_2O_2$ , where "x" is at least 1. In one aspect of the invention, the oxidizers comprise at least  $H_2O_2$  and at least another oxidizer selected from the group consisting of  $O_2$ ,  $O_3$ ,  $NO_x$ , and  $N_2O$ , where "x" is at least 1. Use of more than one of the another oxidizers is of course contemplated, as is use of additional oxidizers.

In the exemplary depicted Fig. 2 example, flow rate of the oxidizer(s) and flow rate of the metal organic precursor(s) are provided to the reactor under some suitable set of conditions effective to deposit a substantially homogenous barium strontium titanate layer 118.

Alternate processing could of course be utilized. Fig. 3 illustrates an alternate embodiment wafer fragment 110a. Like numerals from the first described embodiment are utilized where appropriate, with differences being indicated with the suffix "a" or with different numerals. Some aspect of the rate of flow of the precursor or the oxidizer(s) (i.e., the rate of flow of one

or more oxidizers to the reactor) is changed to affect a change in relative atomic concentration of barium and strontium, for example to deposit a substantially homogenous second portion 122 of barium strontium titanate layer 118a. Accordingly regions 120 and 122 of layer 18 while constituting barium strontium titanate have different relative atomic ratios of barium and strontium. Ratios of barium to strontium in the deposited layer might vary anywhere from 1% to 99% barium versus strontium.

Additional and/or alternate preferred processing can occur in accordance with any of our co-pending U.S. Patent Application Serial No. 09/476,516, filed on January 3, 2000, entitled "Chemical Vapor Deposition Methods Of Forming A High K Dielectric Layer And Methods Of Forming A Capacitor", listing Cem Basceri as inventor; U.S. Patent Application Serial No. 09/580,733, filed on May 26, 2000, entitled "Chemical Vapor Deposition Methods And Physical Vapor Deposition Methods", listing Cem Basceri as inventor; and U.S. Patent Application Serial No. 09/\_\_\_\_\_, filed concurrently herewith, entitled "Chemical Vapor Deposition Methods Of Forming Barium Strontium Titanate Comprising Dielectric Layers, Including Such Layers Having A Varied Concentration Of Barium And Strontium Within The Layer", listing Cem Basceri and Nancy Alzola as inventors. Each of these is hereby fully incorporated by reference.

Preferred total flows of the oxidizers include anywhere from 100 sccm to 4000 sccm, more preferably between 500 sccm and 2000 sccm, and more

preferably between 750 sccm and 1250 sccm. Such flow rates are with respect to an Applied Materials Centura Frame processor. A preferred pressure range is from 100 mTorr to 20 Torr, with a range of from 1 Torr to 6 Torr believed to be most preferred. Susceptor temperature is preferably from 100°C to 700°C, more preferably from 400°C to 700°C, with less than or equal to 550°C being even more preferred, particularly in obtaining continuity in the deposited layer at a thickness at or below 200 Angstroms, and preferably at least down to 50 Angstroms. Most preferably, the susceptor temperature is kept at less than or equal to 550°C during all of the deposit to form the subject layer. An inert gas, such as Ar, is also preferably flowed to the reactor downstream of the oxidizer feeds, and preferably at substantially the same flow rate as the total oxidizer flow rate.

It is expected that  $\text{H}_2\text{O}_2$  would be a stronger oxidizer as compared to  $\text{H}_2\text{O}$ . Without being limited by any theory, it is expected that both  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$  will form  $\text{OH}^-$  during deposition conditions for BST films. Although  $\text{OH}^-$  will behave differently than other oxidizers (such as  $\text{O}_3$ ,  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{N}_2\text{O}$ ) in the presence of BST precursors, its effect is expected to mild and similar to  $\text{N}_2\text{O}$ . By way of example only, and not in any way by way of limitation, use of  $\text{H}_2\text{O}$  and/or  $\text{H}_2\text{O}_2$  as sole oxidizers is expected to increase the atomic percent of titanium in the titanate, and reduce the deposition rate as compared to a 50:50 volumetric ratio control feed of  $\text{O}_2$  and  $\text{N}_2\text{O}$  as oxidizers. Use of a)  $\text{O}_2$  and, b)  $\text{H}_2\text{O}$  and/or  $\text{H}_2\text{O}_2$  in combination in a 1:1

volumetric ratio is expected to decrease titanium incorporation in the titanate, and increase the deposition rate. Utilization of a)  $O_3$  and, b)  $H_2O$  and/or  $H_2O_2$  is also expected to increase the titanium incorporation in the titanate, but reduce the deposition rate.

In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.